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(54) NONAQUEOUS ELECTROLYTE SECONDARY CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous electrolyte secondary cell excellent in cyclic characteristics by providing a positive electrode which is high in capacity, and is prevented from being lowered in cell capacity and the like even after charging/discharging have been cycled.

SOLUTION: A nonaqueous electrolyte secondary cell formed out of at least a positive electrode, an electrolyte layer containing non-aqueous electrolyte, and of a negative electrode capable of occluding/releasing lithium, is provided with a sheathing layer over the surface of the positive electrode. The sheathing layer is composed of ion conductive high polymer, water soluble high polymer, alkaline metallic salt, oxide, and of hydroxide or conductive carbon. As positive electrode active material, for example, lithium contained composite oxide is used. As a practical example, coating for the positive electrode prepared in such a way that LiCoO₂ and conductive graphite are added to the N-methyl pyrrolidone solution of polyvinylidenefluoride, is applied over an Al foil and dried so as to allow the positive electrode to be formed. The sheathing layer is formed in such a way that polyethylene oxide solution is sprayed over the positive electrode.

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CLAIMS

[Claim(s)]

[Claim 1]A nonaqueous electrolyte secondary battery providing an enveloping layer in a positive electrode surface in an electrolyte layer which contains an anode and nonaqueous electrolyte at least, and a nonaqueous electrolyte secondary battery which consists of a negative electrode which can occlusion emit lithium.

[Claim 2]A nonaqueous electrolyte secondary battery characterized by enveloping layers being ion-conductive polymers in claim 1.

[Claim 3]A nonaqueous electrolyte secondary battery characterized by an enveloping layer being a water soluble polymer in claim 1.

[Claim 4]A nonaqueous electrolyte secondary battery characterized by an enveloping layer being alkali metal salt, an oxide, or hydroxide in claim 1.

[Claim 5]A nonaqueous electrolyte secondary battery characterized by an enveloping layer being conductive carbon in claim 1.

[Claim 6]A nonaqueous electrolyte secondary battery characterized by positive active material being a lithium content multiple oxide in claim 1.

[Claim 7]A nonaqueous electrolyte secondary battery characterized by positive active material being a lithium content manganese multiple oxide in claim 6.

[Claim 8]A nonaqueous electrolyte secondary battery, wherein electrolyte salt contained in an electrolyte layer in claim 1 is LiPF_6 .

[Claim 9]A nonaqueous electrolyte secondary battery characterized by an electrolyte layer being a polymers solid electrolyte layer in claim 1.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the nonaqueous electrolyte secondary battery excellent in the cycle characteristic.

[0002]

[Description of the Prior Art]Some are remarkable in progress of the miniaturization of electronic equipment in recent years, slimming down, and a weight saving, and the small weight saving is especially carried out from the desktop type to the laptop type and the notebook type in OA field. In addition, the field of new sized electronic equipment, such as an electronic notebook and an electronic still camera, also appears, and, in addition to the miniaturization of the further conventional hard disk and a floppy disk, development of the memory card which is new memory media is also furthered. Highly efficient-ization has been required also of the rechargeable battery supporting such electric power in the wave of the miniaturization of such electronic equipment, slimming down, and a weight saving. Development of a lithium secondary battery has been quickly furthered in such a request as a high energy density battery which replaces a lead storage battery and a nickel cadmium cell.

[0003]Higher electromotive force is acquired, in the negative electrode active material which constitutes these cells, if a lithium metal is used as an electrode, it will be lightweight and will become easy to carry out densification, and. When the dendrite generated, it had an adverse effect of this disassembling an electrolysis solution and this dendrite grew further by charge and discharge, the anode was reached, and there was a problem of causing the short circuit in a cell. Then, when the lithium alloy was used as a negative electrode, such a problem was eased, but the capacity which can be satisfied as a rechargeable battery was not obtained. For this reason, as negative electrode active material, the occlusion discharge of the lithium could be carried out, using a carbon material with high safety was proposed, and many researches have been made till today.

[0004]For example, using for JP,2-66856,A the charge of a conductive carbon material which burned furfuryl resin at 1100 ** as negative electrode active material is proposed. To JP,61-277515,A. Using for negative electrode active material the charge of a conductive carbon material produced by heat-treating aromatic polyimide at the temperature of not less than 2000 ** under an inert atmosphere is indicated, and using for negative electrode active material what graphitized easy-graphite spheroidal carbon is further indicated by JP,4-1115457,A. Furthermore, the rechargeable battery which used for the electrode the carbon material of the insulation of the poly acene structure which heat-treated phenol

system polymers, or semiconductor nature is indicated by JP,61-77275,A.

[0005]On the other hand as positive active material, transition metal oxides, such as TiS_2 , MoS_2 , and Co_2S_6 , V_2O_5 , MnO_2 , and CoO_2 , Or there are a transition metal charcogen compound etc. and many examples which used the inorganic material as the active material have been studied. . By these days, operating potential shows 4V for high-energy-izing. Multiple oxides which have the layer structure shown by LiMO_2 , such as a lithium cobalt oxide and a lithium nickel oxide, Or the multiple oxide which has the Spinel structure shown by LiM_2O_4 is proposed (JP,63-59507,B, JP,8-21431,B).

[0006]

[Problem(s) to be Solved by the Invention]However, even when an anode uses which active material to a charge-discharge cycle characteristic improving by using a carbon material for a negative electrode, the actual condition is that being used by a severe condition called an oxidation state also results, and the problem of a cycle characteristic is not solved. Use of Li content multiple oxide which is especially the 4V class latest active material makes this problem much more serious. For this reason, in a LiMO_2 and

LiM_2O_4 type active material. Many trials which raise a cycle characteristic have been performed by replacing some transition metals M by other elements (JP,63-211565,A, JP,2-139861,A, JP,2-278661, A). However, it was difficult to raise a cycle characteristic without the fall of initial capacity.

[0007]Therefore, the purpose of this invention is to provide the nonaqueous electrolyte secondary battery which was excellent in the cycle characteristic, when a charging and discharging cycle of after provides the anode in which cell capacity etc. do not fall with high capacity.

[0008]

[Means for Solving the Problem]this invention person found out that a nonaqueous electrolyte secondary battery which was excellent in a cycle characteristic was obtained by providing an enveloping layer in a positive electrode surface, as a result of inquiring in order to attain said purpose. That is, the nonaqueous electrolyte secondary battery according to claim 1 provided an enveloping layer in a positive electrode surface in an electrolyte layer which contains an anode and nonaqueous electrolyte at least, and a nonaqueous electrolyte secondary battery which consists of a negative electrode which can occlusion emit lithium.

[0009]The nonaqueous electrolyte secondary battery according to claim 2 is characterized by enveloping layers being ion-conductive polymers in claim 1.

[0010]The nonaqueous electrolyte secondary battery according to claim 3 is characterized by an enveloping layer being a water soluble polymer in claim 1.

[0011]The nonaqueous electrolyte secondary battery according to claim 4 is characterized by enveloping layers being alkali metal salt, an oxide, and hydroxide in claim 1.

[0012]The nonaqueous electrolyte secondary battery according to claim 5 is characterized by an enveloping layer being conductive carbon in claim 1.

[0013]The nonaqueous electrolyte secondary battery according to claim 6 is characterized by positive active material being a lithium content multiple oxide in claim 1.

[0014]The nonaqueous electrolyte secondary battery according to claim 7 is characterized by positive active material being a lithium content manganese multiple oxide in claim 6.

[0015]The nonaqueous electrolyte secondary battery according to claim 8 is characterized by electrolyte

salt contained in an electrolyte layer being LiPF_6 in claim 1.

[0016]The nonaqueous electrolyte secondary battery according to claim 9 is characterized by an electrolyte layer being a polymers solid electrolyte layer in claim 1.

[0017]Although various reasons a nonaqueous electrolyte secondary battery which was excellent in a cycle characteristic by providing an enveloping layer in a positive electrode surface is obtained are considered, An enveloping layer of a positive electrode surface contributes to suppressing degradation of elution of positive active material by a decomposition product of an electrolyte layer constituent, etc., decomposition, etc. to the minimum, and is considered to suppress degradation of a cycle characteristic by especially one of them.

[0018]In this invention, ion-conductive polymers, a water soluble polymer, alkali metal salt, an oxide, hydroxide, or conductive carbon of an enveloping layer is preferred, and its lithium content multiple oxide is preferred as positive active material. If LiPF_6 is used as electrolyte salt, using a lithium content manganese multiple oxide as positive active material, a remarkable operation effect will be obtained especially. It is effective also when an electrolyte layer is a solid polymer electrolyte.

[0019]Hereafter, composition of a nonaqueous electrolyte secondary battery concerning this invention is explained. positive active material used in a cell of this invention -- carrying out -- transition metal oxides, such as TiS_2 , MoS_2 , and Co_2S_6 , V_2O_5 , MnO_2 , and CoO_2 ,. A transition metal charcogen compound and a complex of these and Li are mentioned. As this Li content multiple oxide, LiCoO_2 , LiNiO_2 , LiFeO_2 , and LiMn_2O_4 . Or a thing which transposed a part of Co of these Li content multiple oxides, nickel, Fe, and Mn to other elements X, That is, although $\text{LiCo}_{1-n}\text{X}_n\text{O}_2$, $\text{LiNi}_{1-n}\text{X}_n\text{O}_2$, $\text{LiFe}_{1-n}\text{X}_n\text{O}_2$, $\text{LiMn}_{2-n}\text{X}_n\text{O}_4$, etc. are mentioned, it is not limited to these. However, especially in these, Li content multiple oxide is effective. It is compounded by calcinating at an elevated temperature by using carbonate, hydroxide, a nitrate, etc. as a starting material, 10 micrometers or less have preferred mean particle diameter, and, as for these Li content multiple oxides, especially 8 micrometers or less are preferred. These active materials may composite-ize several kinds, and may use them.

[0020]An anode using these active materials carries out spreading desiccation on a charge collector, and can produce high-concentration paint liquid which carried out mixture dispersion of a binder and the conducting agent for an active material in solvents, such as dimethylformamide, N-methyl pyrrolidone, and a tetrahydrofuran, if needed. As this dispersion method, a roll mill, a ball mill, a barren mill, etc. are mentioned, and as a coating method, although the wire bar method, the braid coating-machine method, a spray method, etc. are mentioned, it is not limited to these.

[0021]As said binder, electrolysis solution-proof nature is excellent on the assumption that ***** of an active material is not checked, and what has a strong mechanical strength for maintaining an electrode layer is called for. For example, Teflon, polyethylene, nitrile rubber, polybutadiene, Isobutylene isoprene rubber, polystyrene, styrene / butadiene rubber, a nitrocellulose, Cyanoethyl cellulose, polyacrylonitrile, polyvinyl fluoride, Polyvinyl acetate, polyvinylidene fluoride, polyethylene, polystyrene, polypropylene, polytetrafluoroethylene, polymethylmethacrylate, polychloroprene, polyvinyl pyridine, etc. are mentioned. If said conducting agent is a electron conductive material which does not cause a chemical change in a constituted fuel cell subsystem, anything, it will be good and natural graphite, an artificial graphite, etc. will usually be used.

[0022]To not barring movement of lithium and an electrolysis solution, it is stable, an insoluble thing is required, and the construction material, a manufacturing method, etc. are not limited for an enveloping layer provided on an anode. As these examples, ion-conductive polymers, a water soluble polymer, alkali metal salt, an oxide, hydroxide, conductive carbon, etc. are mentioned as mentioned above. Polyethylene oxide which is usually used at a solid polymer electrolyte in the case of ion-conductive polymers, Polymer matrices, such as polypropylene oxide, polyvinylidene fluoride, and polyacrylonitrile, And a method of forming a complex which dissolved electrolyte salt if needed as an enveloping layer by the applying method etc., A method of forming polymerization films, such as vinyl fluoride, an octamethyltetra siloxane, hexamethyl disiloxane, and hexamethyl cyclosiloxane, by plasma CVD is mentioned.

[0023]In the case of a water soluble polymer, polyvinyl alcohol, polyethylene oxide, Hydrolyzate of polypropylene oxide, a polyvinyl pyrrolidone, styrene, and an anhydrous maleate copolymer or its water soluble salt, methyl cellulose, carboxymethyl cellulose or its water soluble salt, polyacrylic acid, or its water soluble salt is mentioned. However, polyvinyl alcohol is more effective and a high thing which has a higher saponification degree has a better degree of polymerization. These are independent, or mix and use two or more kinds. Lithium salt is preferred although lithium salt, sodium salt, ammonium salt, amine salt, etc. are mentioned as water soluble salt.

[0024]These can consider how to form an enveloping layer by applying using polar solvents, such as water and alcohol. In the case of alkali metal salt, an oxide, and hydroxide, a method of applying solution which dissolved these, a method by plasma treatment, etc. are mentioned. In the case of conductive carbon, a method of forming an enveloping layer by the applying method, vacuum deposition, a sputtering technique, etc. is mentioned in conductive carbon used for a conducting agent for the above-mentioned anodes. As for thickness of an enveloping layer formed by these methods, 0.1-50 micrometers is preferred, and especially its 0.5-10 micrometers are preferred.

[0025]As a negative pole material used for a cell of this invention, lithium alloys, such as an alloy of low melting point metals, such as a lithium metal, Pb, Bi, and Sn, and Li and Li-aluminum alloy, a carbonaceous material, etc. are used. Although a baking body of graphite (black lead), pitch coke, synthetic macromolecule, and naturally-occurring polymers is mentioned as carbonaceous negative electrode active material, it is not limited to these. A carbon negative electrode is produced from a carbon body and a binder as mentioned above by a paint which mixed a binder with a carbon material to wet paper-making method or a coating method.

[0026]As a binder of a negative electrode, like an anode, Teflon, polyethylene, nitrile rubber, Polybutadiene, isobutylene isoprene rubber, polystyrene, styrene / butadiene rubber, A nitrocellulose, cyanoethyl cellulose, polyacrylonitrile, Polyvinyl fluoride, polyvinyl acetate, polyvinylidene fluoride, polyethylene, polystyrene, polypropylene, polytetrafluoroethylene, polymethylmethacrylate, polychloroprene, polyvinyl pyridine, etc. are mentioned.

[0027]As a positive-and-negative-poles charge collector used for this invention, for example Stainless steel, platinum, A net and a nonwoven fabric which consist of metal sheets, such as nickel, aluminum, molybdenum, and titanium, a metallic foil, a metallic net, a punching metal, an expanded metal or metal plating textiles, a metal deposition line, a metal content synthetic fiber, etc. are mentioned. Especially, considering electrical conductivity, chemical stability, electrochemical stability, economical efficiency, processability, etc., especially a thing for which aluminum and stainless steel are used is preferred. Aluminum is still more preferred when lightweight nature and electrochemical stability are taken into

consideration.

[0028]As for the surface of a positive electrode collector layer used for this invention, and a negative pole collector layer, it is preferred to have carried out surface roughening. While a touch area of an active material layer becomes large by performing surface roughening, adhesion also improves and it is effective in lowering impedance as a cell. In electrode production using a paint solution, the adhesion of an active material and a charge collector can be greatly raised by performing a surface roughening process. As a surface roughening process, there are polish by emery paper, blast processing, and chemical or electrochemical etching, and, thereby, surface roughening of the charge collector can be carried out.

[0029]In the case of aluminum, as said surface roughening method, blast processing of an etching process (etched aluminum) is preferred in the case of stainless steel respectively. Since aluminum is soft metal, by blast processing, it will not be able to perform an effective surface roughening process and aluminum itself will transform it. On the other hand, the etching process can carry out surface roughening of the surface effectively to mum order, without lowering modification of aluminum and its intensity greatly, and is the most preferred as the surface roughening method of aluminum.

[0030]Although it is nonaqueous electrolyte finally used for this invention, First, as electrolyte salt, LiClO_4 , LiAsF_6 , LiPF_6 , LiBF_4 , LiBr , LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, $\text{LiC}(\text{CF}_3\text{SO}_2)_3$, etc. are mentioned, Especially in LiPF_6 to which decomposition takes place easily, it is effective although not limited in particular. Although electrolytic concentration which should be set up changes with electrodes and electrolysis solutions to be used, 0.1 - 10 mol/l is preferred.

[0031]As a solvent which constitutes an electrolysis solution, for example And a tetrahydrofuran, Ether, such as 2-methyltetrahydrofuran, 1,4-dioxane, and dimethoxyethane; Dimethylformamide, Amide, such as dimethylacetamide; Sulfur compound; dimethyl carbonate, such as nitril; dimethyl sulfoxy sulfolane, such as acetonitrile and benzonitrile, Chain carbonic ester, such as diethyl carbonate, methylethyl carbonate, and methyliso propyl carbonate; although cyclic carbonate, such as ethylene carbonate, propylene carbonate, and butylene carbonate, is mentioned, It is not limited to these, and these may be used independently, and two or more kinds may be mixed and used.

[0032]In this invention, also when using a solid polymer electrolyte, there is a big effect. As a solid polymer electrolyte, as polymer matrices, such as polyethylene oxide, polypropylene oxide, polyvinylidene fluoride, and polyacrylonitrile, A complex which dissolved electrolyte salt in these, Or a solid polymer electrolyte which graft-ized ionic dissociation groups which contain a solvent further, such as a gel bridging body, low-molecular-weight polyethylene oxide, and crown ether, to polymer backbone, a gel solid polymer electrolyte which made the amount polymer of polymers contain said electrolysis solution, etc. are mentioned.

[0033]A separator can also be used in a cell of this invention. It is good to use as a separator what is low resistance and was excellent in solution maintenance to ion migration of an electrolytic solution. As such an example of a separator, a nonwoven fabric filter which consists of polymer fibers, such as glass fiber, a filter, polyester, Teflon, poly chlorofluocarbon, and polypropylene, a nonwoven fabric filter which mixed glass fibers and those polymer fibers, etc. can be mentioned.

[0034]

[Example]

Example 1 Li_2CO_3 and CoCO_3 were mixed by 0.5/1 of mole ratios, and LiCoO_2 was compounded by

calcinating at 900 °C among the air for 5 hours. Polyvinylidene fluoride 3 weight section was dissolved in N-methyl-pyrrolidone 80 weight section, said LiCoO_2 91 weight section and conductive black lead 6 weight section were added to this, mixture dispersion was carried out under the inert atmosphere by the roll mill method, and the paint for anodes was prepared. Applied this on 20-micrometer-thick Al foil using the doctor blade in the atmosphere, it was made to dry for 120 °C and 20 minutes, the ROSUI press was carried out, and the anode of 50 micrometers of thickness was produced. Spray coating of the water / the ethanol (1/1: volume ratio) 5% solution of polyethylene oxide (degree of polymerization 250) was carried out, and the 5-micrometer-thick enveloping layer was formed on the above-mentioned anode.

[0035] Li board was used as a counter electrode, the ethylene carbonate / dimethyl carbonate (5/5: volume ratio) solution 2.0 mol/l of LiPF_6 were used for the anode which provided the above-mentioned enveloping layer as an anode as an electrolysis solution, respectively, and the charge and discharge test was done. In a charge and discharge test, a TOYO SYSTEM TOSCAT3000U type charge-and-discharge measuring device is used, It charged until cell voltage was set to 4.2V with the current density of 0.5 mA/cm², and cell voltage discharged to 3.0V with the current of 0.5 mA/cm² after the pause for 10 minutes, and charge and discharge called the pause for 10 minutes were repeated. The service capacity density (mAh/cm³) of the first stage and a 200 cycle eye was shown in [Table 1].

[0036] Example 2 LiOH and nickel(OH)₂ were mixed by 1.0/1.0 of mole ratios, it calcinated at 800 °C among the air for 24 hours, and LiNiO_2 was compounded. Following resin composition 3 weight section was dissolved in N-methyl-pyrrolidone 80 weight section, said LiNiO_2 91 weight section and conductive black lead 6 weight section were added to this, mixture dispersion was carried out under the inert atmosphere by the roll mill method, and the paint for anodes was prepared. Applied this on 20-micrometer-thick Al foil using the doctor blade in the atmosphere, it was made to dry for 130 °C and 20 minutes, the roll press was carried out, and the anode of 50 micrometers of thickness was produced.

[Resin composition]

- 4-vinylpyridine/2-hydroxyethyl methacrylate (1/3 mol) Copolymer: 100 weight sections - hexamethylene di-isocyanate MEK oxime block (product [made from Sumitomo Beyer Urethane]

BL3175) :5 weight section [0037] On the above-mentioned anode, the doctor blade was used, the N-methyl-pyrrolidone 5% solution of polyvinylidene fluoride was applied, and the 3.5-micrometer-thick enveloping layer was formed. Hereafter, it evaluated like Example 1.

[0038] Example 3 Li_2CO_3 and MnO_2 were mixed by 0.5/2.0 of mole ratios, it calcinated at 800 °C among the air for 12 hours, and LiMn_2O_4 was compounded. Polyvinylidene fluoride 3 weight section was dissolved in N-methyl-pyrrolidone 80 weight section, said LiMn_2O_4 91 weight section and conductive black lead 6 weight section were added, mixture dispersion was carried out under the inert atmosphere by the roll mill method, and the paint for anodes was prepared. Applied this on 20-micrometer-thick Al foil using the doctor blade in the atmosphere, it was made to dry for 120 °C and 20 minutes, the roll press was carried out, and the anode of 50 micrometers of thickness was produced. On this anode, polymerization of the vinyl fluoride was carried out with plasma CVD method, and the 0.7-micrometer-thick enveloping layer was formed. Plasma-CVD conditions were the discharge output 20W, the discharge frequency of 10 MHz, vinyl fluoride flow ³ of 10 cm /, and min, and chamber internal pressure

0.5torr. Hereafter, it was estimated as Example 1 in a similar manner.

[0039]On the anode produced in example 4 Example 3, the solution which carried out the heating and dissolving of the polyvinyl alcohol (degree-of-polymerization 1700 and more than saponification degree 99.3mol%) 2.5 weight section to pure water 80 weight section was applied with the doctor blade, and the 2.5-micrometer-thick enveloping layer was formed. Hereafter, it evaluated like Example 1.

[0040]In example 5 Example 4, it was made to be the same as that of Example 4 except having used hydroxyethyl cellulose instead of polyvinyl alcohol.

[0041]On the anode produced in example 6 Example 3, lithium carbonate was carried out with the sauce target with plasma CVD method, and the 0.5-micrometer-thick enveloping layer was formed. Plasma-CVD conditions were discharge output 50W, discharge frequency [of 10 MHz], and chamber internal pressure 2×10^{-2} torr(s). Hereafter, it was estimated as Example 1 in a similar manner.

[0042]Example 7 polyvinylidene-fluoride 3 weight section was dissolved in N-methyl-pyrrolidone 80 weight section, V_{2O_5} 91 weight section and conductive black lead 6 weight section were added, mixture dispersion was carried out under the inert atmosphere by the roll mill method, and the paint for anodes was prepared. Applied this on 20-micrometer-thick Al foil using the doctor blade in the atmosphere, it was made to dry for 120 ** and 20 minutes, the roll press was carried out, and the anode of 50 micrometers of thickness was produced. After this anode was immersed in the hexane solution which distributed lithium powder with a mean particle diameter of 50 micrometers and being further immersed into the tetrahydrofuran containing 1000 ppm of moisture after reduced pressure drying and rolling, reduced pressure drying was carried out and the enveloping layer of 30-micrometer-thick lithium hydroxide was formed.

[0043]Li board was used as a counter electrode, the ethylene carbonate / dimethyl carbonate (5/5: volume ratio) solution 2.0 mol/l of $LiN(CF_3SO_2)_2$ were used for the anode which provided the above-mentioned enveloping layer as an anode as an electrolysis solution, and the charge and discharge test was done. In a charge and discharge test, a TOYO SYSTEM TOSCAT3000U type charge-and-discharge measuring device is used, Charge until cell voltage is set to 3.7V with the current density of 0.4 mA/cm², and with the current of 0.4 mA/cm² after the pause for 10 minutes. Cell voltage discharged to 2.5V, repeated charge and discharge called the pause for 10 minutes, and measured the service capacity density (mAh/cm³) of the first stage and a 200 cycle eye.

[0044]Example 8 conductivity carbon (Lonza graphite KS- 6) 15 weight section was distributed in the toluene 85 weight section, on the anode produced in Example 3, it applied with the doctor blade and the 10-micrometer-thick enveloping layer was formed. Hereafter, it was estimated as Example 1 in a similar manner.

[0045]Example 9 conductivity carbon (Lonza graphite KS- 6) 15 weight section was distributed in the toluene 85 weight section, on the anode produced in Example 2, it applied with the DOTATA braid and the 8-micrometer-thick enveloping layer was formed. Hereafter, it was estimated as Example 1 in a similar manner. The service capacity density (mAh/cm³) of the first stage and a 200 cycle eye in the above Examples 2-9 was shown in [Table 1].

[0046]Example 10 polyvinylidene-fluoride (PVDF) 3 weight section was dissolved in N-methyl-pyrrolidone 65 weight section, natural graphite 32 weight section was added, mixture dispersion was carried out under the inert atmosphere by the roll mill method, and the paint for negative electrodes was prepared. Applied this on 20-micrometer-thick copper foil using the doctor blade in the atmosphere, it

was made to dry for 120 ** and 20 minutes, the roll press was carried out, and the negative electrode of 50 micrometers of thickness was produced. Next, LiPF_6 20 weight section and ethylene carbonate / diethyl carbonate (5/5: volume ratio) 70 weight section were mixed, and the electrolysis solution was prepared. The mixture solution of polyoxyethylene acrylate 12.8 weight section, trimethyl propane acrylate 0.2 weight section, and the benzoin-iso-propyl-ether 0.02 weight section was added and carried out to this, and the photopolymerization solution was prepared.

[0047]The above-mentioned photopolymerization nature solution was made to permeate the above-mentioned negative electrode and the anode produced in Example 4, it irradiated with the high-pressure mercury-vapor lamp, and the electrolysis solution was solidified. After carrying out heat closure of the three sides, having laminated these and putting a pressure on a power generation element part uniformly, it closed under decompression of the one remaining sides, and the cell was produced. In the charge and discharge test, cell voltage repeated charge and discharge with 10-mA current 3.3-4.2V using the TOYO SYSTEM TOSCAT3000U type charge-and-discharge measuring device. The service capacity of the first stage and the 200 cycle eye in this case was shown in [Table 2].

[0048]In comparative example 1 Example 1, it was made to be the same as that of Example 1 except not having provided an enveloping layer on the anode.

[0049]In comparative example 2 Example 2, it was made to be the same as that of Example 2 except not having provided an enveloping layer on the anode.

[0050]In comparative example 3 Example 2, positive active material was made into $\text{LiNi}_{0.9}\text{CO}_{0.1}\text{O}_2$,

and it was made to be the same as that of Example 2 except not having provided an enveloping layer on the anode. $\text{LiNi}_{0.9}\text{CO}_{0.1}\text{O}_2$ mixed LiOH , $\text{nickel}(\text{OH})_2$, and $\text{Co}(\text{OH})_2$ by the mole ratio of 1.0/0.9/0.1,

and it obtained them by calcinating them for 24 hours at 800 ** among the air.

[0051]In comparative example 4 Example 3, it was made to be the same as that of Example 3 except not having provided an enveloping layer on the anode.

[0052]In comparative example 5 Example 3, positive active material was made into $\text{LiMn}_{1.9}\text{nickel}_{0.1}\text{O}_4$,

and it was made to be the same as that of Example 3 except not having provided an enveloping layer on the anode. $\text{LiMn}_{1.9}\text{nickel}_{0.1}\text{O}_4$ mixed Li_2CO_3 , Mn_2O_3 , and NiCO_3 by the mole ratio of 0.5/0.95/0.9, and

it obtained them by calcinating them for 10 hours at 850 ** among the air.

[0053]In comparative example 6 Example 7, it was made to be the same as that of Example 7 except not having provided an enveloping layer on the anode. The service capacity density (mAh/cm^3) of the first stage and a 200 cycle eye in the above comparative examples 1-6 was shown in [Table 1].

[0054]In comparative example 7 Example 10, it was made to be the same as that of Example 10 except not having provided an enveloping layer on the anode. The service capacity of the first stage and a 200 cycle eye was shown in [Table 2].

[0055]

[Table 1]

放電容量密度 (mA h / c m ³)		
	初期	200サイクル目
実施例 1	3 4 8	3 1 3
実施例 2	5 6 3	4 6 9
実施例 3	3 0 9	2 8 0
実施例 4	3 1 4	2 8 9
実施例 5	3 1 1	2 7 8
実施例 6	3 1 5	2 9 1
実施例 7	2 2 0	2 1 1
実施例 8	3 0 6	2 7 6
実施例 9	5 5 1	4 4 2
比較例 1	3 4 8	2 6 9
比較例 2	5 6 5	1 7 2
比較例 3	5 2 0	3 9 0
比較例 4	3 1 5	2 0 8
比較例 5	2 9 3	2 2 1
比較例 6	2 2 0	1 9 5

[0056]

[Table 2]

放電容量 (mA h)		
	初期	200サイクル目
実施例 10	5 5	4 9
比較例 7	5 5	2 1

[0057]

[Effect of the Invention] By the above explanation, according to this invention, the following effects are acquired so that clearly.

(1) A cycle characteristic can be raised, without reducing other characteristics concerning a cell, since the enveloping layer was provided in the positive electrode surface in claim 1 - the 5 predetermined nonaqueous electrolyte secondary battery.

[0058](2) While becoming possible to pull out effectively the characteristic of the lithium content

multiple oxide as claim 6 positive active material and being able to realize high capacity-ization, an improvement of the cycle characteristic which poses a problem with these active materials can be attained.

[0059](3) Since the lithium content manganese multiple oxide was used as claim 7 positive active material, the nonaqueous electrolyte secondary battery whose cycle characteristic improved substantially can be obtained.

[0060](4) Also when the electrolyte salt contained in claim 8 electrolyte layer is LiPF_6 , the cycle degradation of the capacity resulting from this electrolyte salt can be suppressed to the minimum.

[0061](5) Since claim 9 solid polymer electrolyte is excellent in matching with other battery construction materials, even if it uses this for the component of an electrolyte layer, cell capacity does not fall.

[Translation done.]